

CH353 – Physical Chemistry I
Spring 2013, Unique 52575

Exam 3 – March 8, 2013

Name: Key

Always assume ideal gas unless directed otherwise.

You may use any material that does not have a heartbeat and does not connect to the internet or cellular network.

Honor Code:

“The core values of the University of Texas at Austin are learning, discovery, freedom, leadership, individual opportunity, and responsibility. Each member of the University is expected to uphold these values through integrity, honesty, trust, fairness, and respect toward peers and community.”

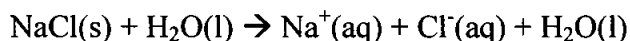
I certify that the work on this exam is entirely my own.

Signature

Date

1. (18 points) Determine if the following statements are true or false.

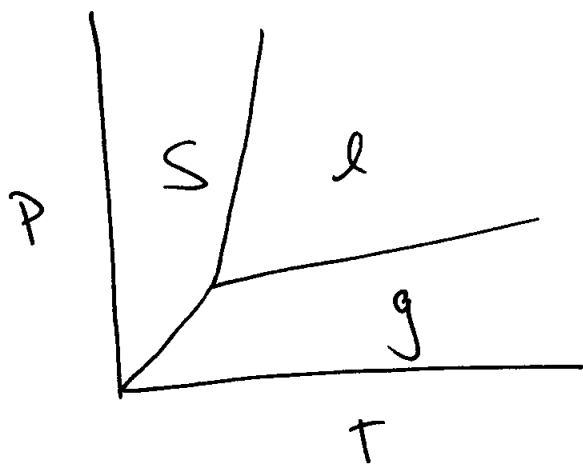
- a. True False Volume and temperature are the natural variables of enthalpy.
- b. True False The conditions for the standard state for the vaporization enthalpy of water is defined as 1 bar and 298 K.
- c. True False The enthalpy of an ideal gas is independent of pressure.
- d. True False For the following reaction:



the chemical potential of the products must be lower than the chemical potential of the reactants.

- e. True False An ideal solution is composed of noninteracting point spheres.

2. (20 points) In many of the simple phase transition diagrams that we have seen in class, the slope of the solid \rightarrow liquid phase boundary is significantly steeper than the solid \rightarrow gas or liquid \rightarrow gas phase boundaries. This steep slope is in fact consistently observed for many different atomic and molecular species. Provide an explanation for this observation in clear comprehensive English (although you may need to incorporate equations into your answer).



$$\frac{dP}{dT} = \frac{\Delta H_{\text{trans}}}{T_{\text{trans}} \Delta V_{\text{trans}}}$$

For the solid \rightarrow gas and liquid \rightarrow gas transition, $\Delta V = V_g - V_{s,l} \approx V_g$, and is usually very large. For the solid \rightarrow liquid transition, $\Delta V = V_l - V_s$ and is usually very small because both condensed phases have small intermolecular distances. This makes the denominator of the Clapeyron equation very small, which makes $\frac{dP}{dT}$ very large.

3. (15 points) a) Determine the change in chemical potential of ice when the pressure is raised from 6 bar to 16 bar at 273 K. $\rho(\text{ice}) = 900 \text{ kg/m}^3$ and $\rho(\text{water}) = 1000 \text{ kg/m}^3$.

$$\mu = \left(\frac{\partial G}{\partial n} \right)_{T,P} \quad \left(\frac{\partial (G/n)}{\partial P} \right)_T = V_m$$

$$\Rightarrow \left(\frac{\partial \mu}{\partial P} \right) = V_m ; \Delta \mu = V_m \Delta P = \frac{(FW)}{\rho} \Delta P$$

$$\Delta \mu(\text{ice}) = \left(\frac{18 \times 10^{-3} \text{ kg/mol}}{900 \text{ kg/m}^3} \right) (10^6 \text{ J/m}^3) = 20 \text{ J/mol}$$

$$\Delta \mu(\text{water}) = \left(\frac{18 \times 10^{-3} \text{ kg/mol}}{1000 \text{ kg/m}^3} \right) (10^6 \text{ J/m}^3) = 18 \text{ J/mol}$$

b) Determine the change in chemical potential of solid CO_2 when the pressure is raised from 6 bar to 16 bar at 273 K. $\rho(\text{CO}_{2(s)}) = 250 \text{ kg/m}^3$ and $\rho(\text{CO}_{2(l)}) = 235 \text{ kg/m}^3$.

$$\Delta \mu(\text{solid}) = \left(\frac{44 \times 10^{-3} \text{ kg/mol}}{250 \text{ kg/m}^3} \right) (10^6 \text{ J/m}^3) = 176 \text{ J/mol}$$

$$\Delta \mu(\text{liquid}) = \left(\frac{44 \times 10^{-3} \text{ kg/mol}}{235 \text{ kg/m}^3} \right) (10^6 \text{ J/m}^3) = 187 \text{ J/mol}$$

c) Explain any differences between your answers in parts a and b.

$V_m(\text{liquid}) < V_m(\text{solid})$ in water, so $\Delta \mu(\text{solid}) > \Delta \mu(\text{liquid})$. This means that ice changes more rapidly than water when pressure is applied. The reverse is true for CO_2 .

4. (25 points) 10 g of ice at 0°C is placed into an insulated (i.e. adiabatic) thermos. 10 g of water with a temperature of 25°C is added, and the thermos is sealed at a constant pressure of 1 atm.

$$C_p(\text{solid}) = 36 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$C_p(\text{liquid}) = 75.3 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$\Delta H_{\text{fus}} = 6.02 \text{ kJ mol}^{-1}$$

$$S^\circ(\text{liquid}, 298 \text{ K}) = 70 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$n(\text{ice}) = n(\text{water}) = 0.556 \text{ moles}$$

a) What is the final temperature of the water in the thermos?

heat lost from the water is gained by the ice

$$\Delta H_{\text{TOT}} = 0$$

$$\text{heat to melt ice: } q = n \Delta H_{\text{fus}} = (0.556 \text{ moles})(6020 \text{ J/mol}) = \underline{3311 \text{ J}}$$

$$\text{heat to cool water: } q = n C_p(\text{water}) \Delta T = (0.556 \text{ moles})(75.3 \text{ J/Kmol})(-25 \text{ K}) = \underline{-1047 \text{ J}}$$

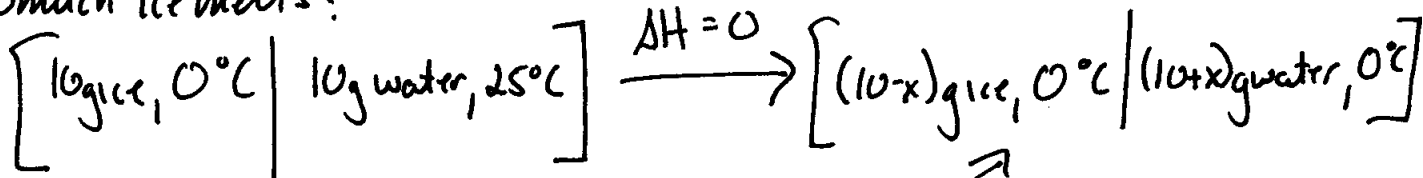
So more heat is required to melt all the ice than to cool all the water to 0°C.

So some ice melts, and the final temperature = 0°C.

$$\boxed{T_f = 0^\circ \text{C}}$$

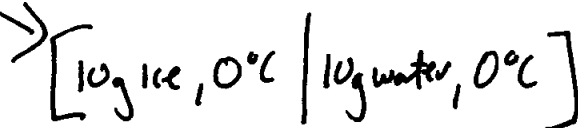
b) Determine ΔS_{sys} , ΔS_{sur} , and ΔS_{total} for this process.

How much ice melts?



① cool water

② melt ice



$$\Delta H_{\text{cool}} + \Delta H_{\text{melt}} = 0 ; n(\text{water}) C_p(\text{water}) \Delta T + \frac{x}{18 \text{ g/mol}} \Delta H_{\text{fus}} = 0$$

$$x = \frac{-(18 \text{ g/mol})(n_{\text{water}})(C_{p\text{water}}) \Delta T}{\Delta H_{\text{fus}}} = \frac{-18 \text{ g/mol}(0.556 \text{ mol})(75.3 \text{ J/Kmol})(-25 \text{ K})}{6020 \text{ J/mol}}$$

$$x = 3.13 \text{ g}$$

$$n_{\text{melt}} = 0.174 \text{ moles}$$

See next page

$$\Delta S_{\text{sys}} = \Delta S_{\text{melt}} + \Delta S_{\text{liquid}}$$

$$\Delta S_{\text{melt}} = \frac{q_{\text{melt}}}{T} = \frac{n \Delta H_{\text{fus}}}{T} = \frac{(0.174 \text{ mol}) (6020 \text{ J/mol})}{273 \text{ K}}$$

$$\Delta S_{\text{melt}} = 3.84 \text{ J/K}$$

$$\Delta S_{\text{liquid}} = n (C_p(\text{liquid})) \ln\left(\frac{T_f}{T_i}\right) = (0.556 \text{ mol}) (75.3 \text{ J/Kmol}) \ln\left(\frac{273 \text{ K}}{296 \text{ K}}\right)$$

$$\Delta S_{\text{liquid}} = -3.67 \text{ J/K}$$

$$\Delta S_{\text{sys}} = 3.84 \text{ J/K} + (-3.67 \text{ J/K})$$

$$\Delta S_{\text{sys}} = 0.17 \text{ J/K}$$

$$\Delta S_{\text{surr}} = 0 \quad (\text{adiabatic})$$

$$\Delta S_{\text{TOT}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}} = 0.17 \text{ J/K}$$

5. (22 points) a) Derive a general expression for the volume dependence of the internal energy, U , of an ideal gas while held at constant temperature.

$$\left(\frac{\partial U}{\partial V}\right)_T = ? \quad dU = TdS - PdV$$

$$\text{divided by } dV: \frac{dU}{dV} = T \frac{dS}{dV} - P$$

$$\text{Impose } \Delta T = 0: \left(\frac{\partial U}{\partial V}\right)_T = T \left(\frac{\partial S}{\partial V}\right)_T - P$$

$$\text{Maxwell Relation: } \left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$$

$$\text{Substitute: } \boxed{\left(\frac{\partial U}{\partial V}\right)_T = T \left(\frac{\partial P}{\partial T}\right)_V - P}$$

$$\text{Ideal gas: } P = \frac{nRT}{V}$$

$$\frac{dP}{dT} = \frac{nR}{V}$$

$$\Rightarrow \left(\frac{\partial U}{\partial V}\right)_T = \frac{TnR}{V} - P$$

$$\boxed{\left(\frac{\partial U}{\partial V}\right)_T = P - P = 0}$$

b) Derive an expression for the volume dependence of the internal energy, U , of a van der Waals gas while held at constant temperature.

↓
This is perfectly general, start here

$$P = \frac{RT}{V_m - b} - \frac{a}{V_m^2} \quad ; \quad \frac{dP}{dT} = \frac{R}{V_m - b}$$

$$\left(\frac{\partial U}{\partial V}\right)_T = T \left(\frac{R}{V_m - b}\right) + \left(\frac{RT}{V_m - b} + \frac{a}{V_m^2}\right) = \frac{a}{V_m^2}$$

$$\text{So } \boxed{\left(\frac{\partial U}{\partial V}\right)_T = \frac{a}{V_m^2}} \quad \text{for a van der Waals gas}$$